

## Toxicity of Six Bird Control Chemicals to Aquatic Organisms

L. L. Marking<sup>1</sup> and J. H. Chandler, Jr.<sup>2</sup>

*U.S. Fish and Wildlife Service, <sup>1</sup>National Fishery Research Laboratory, P.O. Box 818, La Crosse, WI 54601; <sup>2</sup>Southeastern Fish Control Laboratory, P.O. Box 9, Warm Springs, GA 31830*

The U.S. Fish and Wildlife Service (FWS) has supported research on control methods for nuisance birds, mammals, plants, and fish. Although chemical agents have shown great promise, resource managers and regulatory agencies must be assured that these materials are safe to man and the environment. Standardized toxicity tests are conducted to demonstrate the effectiveness of candidate compounds on target organisms and their safety to nontarget organisms (LENNON 1967).

Blackbirds are a common problem and often congregate in huge flocks that threaten agricultural crops. In addition, their roosting sites may serve as foci for human disease outbreaks.

Avian control chemicals developed or being tested by the FWS<sup>1</sup> Denver Wildlife Research Center (DWRC) include PA-14 ( $\alpha$ -alkyl[C<sub>11</sub>-C<sub>15</sub>]-omega-hydroxypoly[oxyethylene]), a surfactant avian stressing agent; 4-AP (4-aminopyridine), a frightening agent; methiocarb (Mesurol®, 3,5-dimethyl-4-[methylthio]phenol methylcarbamate), a repellent; DRC-1339 (3-chloro-4-methylbenzenamine hydrochloride), a bait toxicant; and two dermally applied candidate toxicants, DRC-1347 (3-chloro-4-methyl benzenamine) and DRC-2698 (N-[3-chloro-4-methylphenyl]acetamide). The toxicity of these materials to representative aquatic organisms was determined in this study as part of the Service's testing program to provide information on possible effects of their use or accidental application in aquatic habitats.

SCHAFER & MARKING (1975) reported that 4-AP was nontoxic to five avian and two fish species at suggested treatment concentrations. INGLIS et al. (1967)<sup>1</sup> studied the toxicity of several of these compounds to three species of fish, and WALKER et al. (1979) determined the toxicity of DRC-1339 to shrimp and crabs. However, little information is available on possible adverse effects of these materials on freshwater aquatic organisms.

The objectives of this study were to (1) determine the toxicity of six bird control compounds to selected nontarget aquatic organisms, (2) evaluate potential adverse effects of these materials on eggs and larvae of frogs, and (3) develop information needed in

<sup>1</sup>Unpublished: U.S. Fish and Wildlife Service, Patuxent Wildlife Research Center, Maryland.

applications to obtain or maintain registrations with the Environmental Protection Agency. The study was funded by the DWRC's Section of Bird Damage Control.

## MATERIALS AND METHODS

Technical grades of the avian control chemicals were furnished by the DWRC or by the manufacturers. Test materials were dissolved in acetone or water to prepare concentrated stock solutions. Quantities of these stock solutions were volumetrically added to the water in each of the test vessels to yield desired concentrations. The water in each vessel was then carefully stirred to ensure adequate mixing without injury to test organisms. Scientific names of the test species are given in Tables 1-6.

The static tests were conducted according to the recommendations of the ASTM COMMITTEE E-35 ON PESTICIDES (1980) with minor modifications. The test water, except that used for water fleas, was spring water reconstituted with minerals to yield a total hardness of about 24 mg/L as  $\text{CaCO}_3$ . Water fleas were exposed in reconstituted water with a hardness of about 40 mg/L as  $\text{CaCO}_3$ . Most tests were conducted in either 3 or 15 L of water in glass jars with capacities of 3.78 L (1 gal) or 18.9 L (5 gal). Tests with water fleas were conducted in 500 mL of water in 600-mL beakers.

Water fleas were reared in the laboratory; glass shrimp and crayfish were cultured in earthen ponds at the Warm Springs (Georgia) National Fishery Hatchery. The other test species were obtained from small streams and rivers near Warm Springs. They were then transported to the laboratory and held for at least 3 days before exposure.

Egg clusters of the southern leopard frog were collected from ponds at the Warm Springs hatchery within 16 h after deposition. A single egg mass was used for each of the tests. Egg masses were gently teased into approximately equal clusters, which were then placed in individual test vessels at 16°C. After the test chemicals were added, the eggs remained in the test vessels until they hatched or until development had ceased. Percent hatch and survival were recorded.

Temperatures were maintained at 12, 16, or 22°C by immersing the test vessel in water baths equipped with water chilling units or heaters.

The method of LITCHFIELD & WILCOXON (1949) was used to determine  $\text{LC}_{50}$  and  $\text{EC}_{50}$  values (concentrations calculated to produce 50% mortality or, in water fleas, 50% immobility in 48-h exposures) and the 95% confidence intervals for each test group.

Table 1. Toxicity of PA-14 to Various Aquatic Invertebrates and Frog Larvae in Static Tests.

Species and life stage	Temp (°C)	LC <sub>50</sub> and 95% confidence interval (mg/L)		
		6 h	24 h	96 h
Scud, adult ( <u>Hyalella azteca</u> )	16	6.6 (4.9-8.9)	4.5 (2.5-8.0)	1.4 (1.1-1.8)
Glass shrimp, juvenile ( <u>Palaemonetes kadiakensis</u> )	12	>50	32 (23-44)	7.8 (6.0-10)
Glass shrimp, juvenile	22	35 (23-53)	17 (13-23)	1.7 (1.0-2.8)
Crayfish, juvenile ( <u>Procambarus acutus acutus</u> )	12	>400	280 (210-370)	40 (32-51)
Crayfish, juvenile	16	>350	80 (61-110)	44 (39-50)
Damselfly, nymph ( <u>Ischnura</u> sp.)	16	---	>600	400 (260-590)
Dragonfly, nymph ( <u>Didymops</u> sp.)	16	---	---	>100
Mayfly, nymph ( <u>Isorychnia</u> sp.)	12	180 (140-230)	17 (15-20)	12 (8.8-17)

Table 1. (cont'd)

Species and life stage	Temp (°C)	LC <sub>50</sub> and 95% confidence interval (mg/L)		
		6 h	24 h	96 h
Mayfly, nymph	16	83 (79-88)	64 (59-70)	5.2 (4.1-6.7)
Caddisfly, larvae ( <u>Hydropsyche</u> sp.)	12	>60	15 (13-17)	2.0 (1.3-3.2)
Caddisfly, larvae	16	40 (29-56)	13 (11-15)	1.9 (1.2-3.0)
Backswimmers, adult ( <u>Notonecta</u> sp.)	16	3.0 (2.6-3.4)	2.3 (2.1-2.6)	1.9 (1.6-2.3)
Backswimmers, adult ( <u>Buenoa</u> sp.)	16	4.2 (3.8-4.7)	4.2 (3.8-4.7)	3.1 (2.8-3.4)
River horn snail, adult ( <u>Oxytrema catenaria</u> )	12	---	18 (12-29)	6.0 (4.1-8.7)
River horn snail, adult	16	---	20 (17-23)	5.5 (4.5-6.7)
River horn snail, adult	22	---	7.0 (5.1-9.5)	5.2 (3.6-7.5)

Table 1. (cont'd)

Species and life stage	Temp (°C)	LC50 and 95% confidence interval (mg/L)			
		6 h	24 h	96 h	
Buckley's filter clam ( <u>Elliptio buckleyi</u> )	16	---	>200	58 (46-74)	
Asiatic clam, adult ( <u>Corbicula manilensis</u> )	12	---	>500	250 (210-290)	
Asiatic clam, adult	16	---	550 (400-760)	130 (110-150)	
Asiatic clam, adult	22	---	300 (140-640)	3.6 (3.1-4.3)	
Frog, larvae ( <u>Rana sphenocéphala</u> )	12	7.5 (6.4-8.8)	7.5 (6.3-9.0)	5.9 (5.3-6.5)	
Frog, larvae	16	9.8 (8.6-11)	4.5 (4.2-4.7)	4.2 (3.6-4.7)	
Frog, larvae	22	3.2 (2.3-4.7)	2.6 (2.0-3.4)	2.3 (1.8-2.9)	

Table 2. Toxicity of 4-AP to Aquatic Invertebrates and Frog Larvae in Static Tests

Species and life stage	Temp (°C)	LC <sub>50</sub> and 95% confidence interval (mg/L)		
		6 h	24 h	96 h
Water fleas, juvenile ( <u>Daphnia magna</u> )	21	24 (19-30)	17 (14-20)	3.2 (2.3-4.5)
Glass shrimp, juvenile ( <u>Palaemonetes kadiakensis</u> )	16	47 (32-70)	3.3 (2.3-4.6)	0.37 (0.25-0.56)
Crayfish, juvenile ( <u>Procambarus acutus acutus</u> )	16	>60	14 (11-18)	2.2 (1.7-2.8)
Mayfly, nymph ( <u>Isonychia</u> sp.)	12	24 (20-28)	5.3 (3.9-7.2)	0.58 (0.45-0.74)
Caddisfly, larvae ( <u>Hydropsyche</u> sp.)	16	99 (78-130)	30 (21-41)	15 (9.8-22)
River horn snail, adult ( <u>Oxytrema catenaria</u> )	16	---	>100	62 (53-73)
Asiatic clam, adult ( <u>Corbicula manilensis</u> )	16	---	78 (69-88)	45 (40-50)
Frog, larvae ( <u>Rana sphenocphala</u> )	16	>30	7.2 (6.6-7.8)	2.4 (2.0-2.9)

Table 3. Toxicity of Methiocarb to Aquatic Invertebrates and Frog Larvae in Static Tests.

Species and life stage	Temp (°C)	LC50 and 95% confidence interval (mg/L)		
		6 h	24 h	96 h
Glass shrimp, juvenile ( <u>Palaemonetes kadiakensis</u> )	16	>0.80	0.42 (0.34-0.51)	0.11 (0.10-0.13)
Crayfish, juvenile ( <u>Procambarus acutus acutus</u> )	16	18 (13-25)	3.7 (2.9-4.6)	1.3 (0.93-1.9)
Mayfly, nymph ( <u>Isonychia</u> sp.)	12	1.3 (0.85-1.8)	0.018 (0.011-0.030)	0.007 (0.005-0.011)
Caddisfly, larvae ( <u>Hydropsyche</u> sp.)	16	0.49 (0.41-0.58)	0.20 (0.12-0.32)	0.014 (0.009-0.023)
River horn snail, adult ( <u>Oxytremna catenaria</u> )	16	>1.0	0.14 (0.13-0.16)	0.10 (0.088-0.11)
Asiatic clam, adult ( <u>Corbicula manilensis</u> )	16	---	13 (9.5-16)	8.8 (6.2-13)
Frog, larvae ( <u>Rana sphenoccephala</u> )	16	9.7 (8.8-11)	8.5 (7.9-9.2)	8.7 (7.8-9.6)

Table 4. Toxicity of DRC-1339 to Aquatic Invertebrates and Frog Larvae in Static Tests.

Species and life stage	Temp (°C)	LC <sub>50</sub> and 95% confidence interval (mg/L)		
		6 h	24 h	96 h
Water fleas, juvenile ( <u>Daphnia magna</u> )	21	19 (15-25)	13 (9.3-18)	1.6 (1.0-2.3)
Glass shrimp, juvenile ( <u>Palaemonetes kadiakensis</u> )	16	31 (25-38)	25 (21-29)	6.1 (4.7-7.9)
Crayfish, juvenile ( <u>Procambarus acutus acutus</u> )	16	>30	17 (15-20)	15 (11-21)
Mayfly, nymph ( <u>Isonychia</u> sp.)	12	>100	18 (16-21)	12 (9.7-14)
Caddisfly, larvae ( <u>Hydropsyche</u> sp.)	16	40 (29-54)	36 (25-50)	6.5 (4.9-8.6)
River horn snail, adult ( <u>Oxytrema catenaria</u> )	16	>25	22 (19-25)	6.7 (5.7-7.9)
Asiatic clam, adult ( <u>Corbicula manilensis</u> )	16	---	>25	18 (17-20)
Frog, larvae ( <u>Rana sphenocéphala</u> )	16	>100	63 (60-66)	44 (42-47)



Table 5. Toxicity of DRC-1347 to Aquatic Invertebrates and Frog Larvae in Static Tests

Species and life stage	Temp (°C)	LC50 and 95% confidence interval (mg/L)		
		6 h	24 h	96 h
Glass shrimp, juvenile ( <u>Palaemonetes kadiakensis</u> )	16	15 (12-20)	9.0 (8.8-9.1)	4.5 (3.6-5.6)
Crayfish, juvenile ( <u>Procambarus acutus acutus</u> )	16	38 (32-45)	25 (18-34)	8.8 (8.2-9.5)
Mayfly, nymph	12	22 (20-24)	12 (11-14)	3.8 (2.9-5.1)
Caddisfly, larvae ( <u>Hydropsyche</u> sp.)	16	31 (23-40)	20 (17-23)	7.5 (5.0-11)
River horn snail, adult ( <u>Oxytrema catenaria</u> )	16	>100	32 (26-38)	16 (12-21)
Asiatic clam, adult ( <u>Corbicula manilensis</u> )	16	---	64 (55-75)	62 (53-72)
Frog, larvae ( <u>Rana sphenoccephala</u> )	16	47 (46-49)	41 (40-42)	32 (30-34)

Table 6. Toxicity of DRC-2698 to Aquatic Invertebrates and Frog Larvae in Static Tests

Species and life stage	Temp (°C)	LC <sub>50</sub> and 95% confidence interval (mg/L)		
		6 h	24 h	96 h
Glass shrimp, juvenile ( <u>Palaemonetes kadiakensis</u> )	16	>100	70 (57-87)	39 (34-44)
Crayfish, juvenile ( <u>Procambarus acutus acutus</u> )	16	---	>100	94 (79-110)
Mayfly, nymph ( <u>Isonychia</u> sp.)	12	60 (47-77)	44 (35-55)	5.5 (3.9-7.9)
Caddisfly, larvae ( <u>Hydropsyche</u> sp.)	16	>100	95 (65-140)	4.5 (3.0-6.5)
River horn snail, adult ( <u>Oxytrema catenaria</u> )	16	---	120 (110-120)	38 (30-48)
Asiatic clam, adult ( <u>Corbicula manilensis</u> )	16	---	>800	96 (88-110)
Frog, larvae ( <u>Rana sphenoccephala</u> )	16	---	---	>30

## RESULTS

PA-14. PA-14 was toxic to crustaceans, insects, snails, clams, and frog larvae and, under some test conditions, 96-h LC<sub>50</sub>'s were less than 10 mg/L for these organisms (Table 1). Exposures under other test conditions resulted in 96-h LC<sub>50</sub>'s greater than 10 mg/L for crayfish, mayfly nymphs, and a native clam, and greater than 100 mg/L for damselfly and dragonfly nymphs and Asiatic clams.

Water temperature influenced the toxicity of PA-14 to some organisms, but not to others. For example, toxicity to glass shrimp, mayfly nymphs, Asiatic clams, and frog larvae increased as temperatures increased to 16 and 22°C whereas toxicity to crayfish, caddisfly larvae, and river horn snails was not significantly affected by temperatures (Table 1).

4-AP. Glass shrimp and mayfly nymphs were highly sensitive to 4-AP; 96-h LC<sub>50</sub>'s were 0.37 and 0.58 mg/L, respectively (Table 2). River horn snails and Asiatic clams were the most resistant (96-h LC<sub>50</sub>'s, 62 and 45 mg/L); however, the snails were visibly affected at concentrations lower than the LC<sub>50</sub>. Although they did not die in the 96-h exposure, they were unable to right themselves when they were dislodged and were unable to cling to sidewalls of the test vessel.

Methiocarb. Methiocarb was more toxic than PA-14 and 4-AP to crustaceans, aquatic insects, and river horn snails. The 96-h LC<sub>50</sub>'s ranged from 0.007 for mayfly nymphs to 1.3 mg/L for juvenile crayfish (Table 3). Asiatic clams and frog larvae were more resistant to methiocarb (96-h LC<sub>50</sub>'s, 8.8 and 8.7 mg/L) than the other aquatic organisms.

DRC-1339. The avicide DRC-1339 was more toxic than 4-AP to water fleas (48-h EC<sub>50</sub>'s = 1.6 and 3.2 mg/L listed in the 96-h column) (Tables 2 and 4). The reaction of other aquatic organisms (except Asiatic clams) was similar to that of PA-14. The 96-h LC<sub>50</sub>'s for glass shrimp, caddisfly larvae, and snails ranged from 6.1 to 6.7 mg/L, and those for mayfly nymphs, crayfish, and Asiatic clams from 12 to 18 mg/L.

DRC-1347 and DRC-2698. The toxicity of these metabolites of DRC-1339 varied among the test organisms (Tables 5 and 6). DRC-1347 was significantly more toxic than DRC-1339 to crayfish and mayfly nymphs, but significantly less toxic to river horn snails, Asiatic clams, and frog larvae. DRC-2698 was significantly more toxic than DRC-1339 to mayfly nymphs, but significantly less toxic to glass shrimp, crayfish, river horn snails, and Asiatic clams.

Frog Egg Tests. Hatching of leopard frog eggs in control lots required 9 to 11 days. The percentages of undeveloped eggs or dead larvae remaining in the gelatinous envelope of embryos which hatched, and of larvae which survived after hatching were noted. Except for DRC-2698, concentrations that permitted 95% hatching success differed from those that permitted 95% larval survival.

(Table 7). Although many of the compounds permitted hatching at high concentrations, the percentage of larvae that survived after hatching was reduced. Over 95% of the larvae survived exposures to 15 mg/L of DRC-1347 and at 30 mg/L of DRC-2698. Methiocarb and 4-AP were the most detrimental to larval survival (95% of the larvae survived 2.0- and 1.0-mg/L exposures). There was 95% survival of larvae exposed to 4.0 mg/L of PA-14 and 5.0 mg/L of DRC-1339.

Table 7. Effects of Bird Control Chemicals on Hatching Success and Larval Survival of the Leopard frog, Rana sphenoccephala, in Static Tests at 16°C

Compound	Concentrations (mg/L) resulting in			
	Hatching success		Larval survival	
	>95%	<5%	>95%	<5%
P-14	6.0	10	4.0	8.0
4-AP	--	<10 <sup>a</sup>	1.0	2.0
Methiocarb	15	25	2.0	8.0
DRC-1339	80	>100	5.0	40
DRC-1347	80	100	15	20
DRC-2698	30	>100	30	40

<sup>a</sup>10 mg/L = highest concentration used.

#### REFERENCES

- ASTM COMMITTEE E-35 ON PESTICIDES: Standard practice for conducting acute toxicity tests with fishes, macroinvertebrates, and amphibians, E 729-80 in Annual Book of ASTM Standards. Philadelphia, Pennsylvania. (1980).
- LENNON, R. E.: Prog. Fish-Cult. 29, 187 (1967).
- LITCHFIELD, J. T., JR., and F. WILCOXON: J. Pharmacol. Exp. Ther. 96, 99 (1949).
- SCHAFER, E. W., JR., and L. L. MARKING: J. Wildl. Manage. 39, 807 (1975).
- WALKER, W. W., A. R. LAWLER, and W. O. BURKE: Bull. Environ. Contam. Toxicol. 21, 643 (1979).

Accepted April 7, 1981